Journal of the Mechanics and Physics of Solids 95 (2016) 64–91

Contents lists available at ScienceDirect

Journal of the Mechanics and Physics of Solids

journal homepage: www.elsevier.com/locate/jmps

Stress induced phase transitions in silicon

M. Budnitzki*, M. Kuna

TU Bergakademie Freiberg, Institute of Mechanics and Fluid Dynamics, Lampadiusstr. 4, 09599 Freiberg, Germany

A R T I C L E I N F O

Article history:
Received 8 May 2015
Received in revised form
7 March 2016
Accepted 21 March 2016
Available online 25 March 2016

Keywords:
Silicon
Constitutive model
Stress induced phase transition
Indentation
Contact loading

A B S T R A C T

Silicon has a tremendous importance as an electronic, structural and optical material. Modeling the interaction of a silicon surface with a pointed asperity at room temperature is a major step towards the understanding of various phenomena related to brittle as well as ductile regime machining of this semiconductor. If subjected to pressure or contact loading, silicon undergoes a series of stress-driven phase transitions accompanied by large volume changes. In order to understand the material's response for complex non-hydrostatic loading situations, dedicated constitutive models are required. While a significant body of literature exists for the dislocation dominated high-temperature deformation regime, the constitutive laws used for the technologically relevant rapid low-temperature loading have severe limitations, as they do not account for the relevant phase transitions. We developed a novel finite deformation constitutive model set within the framework of thermodynamics with internal variables that captures the stress induced semiconductor-to-metal (cd–Si → β–Si), metal-to-amorphous (β–Si → a–Si) as well as amorphous-to-amorphous (a–Si → hda–Si, hda–Si → a–Si) transitions. The model parameters were identified in part directly from diamond anvil cell data and in part from instrumented indentation by the solution of an inverse problem. The constitutive model was verified by successfully predicting the transformation stress under uniaxial compression and load–displacement curves for different indenters for single loading–unloading cycles as well as repeated indentation. To the authors' knowledge this is the first constitutive model that is able to adequately describe cyclic indentation in silicon.

1. Introduction

1.1. Experimental results

Minomura and Drickamer (1962) were the first to note that high pressure loading of silicon is accompanied by a change in conductivity, which they attributed to a semiconductor-to-metal phase transition. This conclusion was later confirmed by Jamieson (1963) using X-ray diffraction. Since this pioneering work as many as 12 other solid phases of Si were discovered (Hu et al., 1986; Mcmahon and Nelmes, 1993; Mcmahon et al., 1994; Domnich and Gogotsi, 2002). Experiments employing diamond anvil cells in order to impose hydrostatic loading conditions have revealed that diamond-cubic Si (cd-Si, space group $Fd3m$) transforms to the (metallic) β-tin structure (β-Si, space group $I4_1/amd$) at ~11.3 GPa, leading to ~20%

Abbreviations: KKT, Karush–Kuhn–Tucker; Si, silicon; cd-Si, diamond-cubic silicon; β-Si, β-tin phase of silicon; a-Si, amorphous silicon; hd-Si, high-density pseudo-phase of silicon; ld-Si, low-density pseudo-phase of silicon

* Corresponding author.

http://dx.doi.org/10.1016/j.jmps.2016.03.017
0022-5096/© 2016 Elsevier Ltd. All rights reserved.

Nomenclature

a, b, b'	model parameters
$\hat{\boldsymbol{B}}_\text{i}$	inelastic left Cauchy–Green stretch tensor
d	model parameter
$\hat{\boldsymbol{D}}_\text{i}$, $\hat{\mathfrak{D}}_\text{i}$	inelastic stretching tensor, its deviator
$\boldsymbol{E}^\text{H}$, $\mathfrak{E}^\text{h}$	spatial Hencky strain tensor, its deviator
$\boldsymbol{E}_\text{e}^\text{H}$, $\hat{\mathfrak{E}}_\text{e}^\text{H}$	elastic Hencky strain tensor, its deviator
$\hat{\boldsymbol{E}}_\text{i}^\text{h}$, $\hat{\mathfrak{E}}_\text{i}^\text{h}$	inelastic Hencky strain tensor, its deviator
$\boldsymbol{F}_\text{e}$, $\boldsymbol{F}_\text{i}$	elastic, inelastic deformation “gradient”
J_i	determinant of $\boldsymbol{F}_\text{i}$
$\hat{\boldsymbol{M}}_\text{e}$, $\hat{\mathfrak{M}}_\text{e}$	Mandel stress tensor, its deviator
$\hat{\boldsymbol{M}}_\text{e}^\text{eff}$, $\hat{\mathfrak{M}}_\text{e}^\text{eff}$	effective Mandel stress tensor, its deviator
p, $\wp$	true pressure, Kirchhoff pressure
$\hat{p}_\text{e}$, $\hat{p}_\text{e}^\text{eff}$	Mandel type pressure, effective pressure
$\wp_\text{b}$	Kirchhoff type backpressure
$\wp_\text{t}$	model parameter
$\boldsymbol{S}$, $\mathfrak{S}$	true stress tensor, its deviator
S_q	von Mises equivalent stress
$\boldsymbol{T}$, $\mathfrak{T}$	Kirchhoff stress tensor, its deviator
β_p	thermodynamic force conjugate to γ_p
γ_p	internal variable
κ	bulk modulus
$\dot{\lambda}$	“plastic” multiplier
ν	Poisson's ratio
ν_tr	inelastic volumetric strain
ν_tr^max	max. value of ν_tr over the loading history
ν_tr^hd	volume change during ld–Si → hd–Si
ρ_0	density in reference configuration
$\hat{\rho}$	density in intermediate configuration
τ_0	model parameter

densification (Welber et al., 1975; Hu et al., 1986). At room temperature,[1] this transition is not reversible and a mixture of crystalline phases (Si-XII, Si-III) denoted as mc-Si or amorphous silicon (a-Si) are formed for slow and rapid decompression, respectively (Domnich and Gogotsi, 2002; Juliano et al., 2003). If initially amorphous silicon is compressed, a metallic amorphous phase (hda-Si) is formed, which unloads to a-Si (Shimomura et al., 1974). This transformation is reversible.

A new solid phase underneath indents in silicon was reported as early as 1972 by Eremenko and Nikitenko, but its importance was not recognized until Gerk and Tabor (1978) observed that the indentation hardness, i.e. the mean pressure under the indenter tip, of silicon corresponds to the pressure for the semiconductor-to-metal transition. They concluded that phase transformation is the governing mechanism for inelastic deformation of silicon under contact loading. Nanoindentation studies with various indenter-shapes[2] have shown that non-hydrostatic conditions lower the transformation stress, which is in accordance with theoretical considerations by Gilman (1993a) as well as various atomistic studies (cf. Lee et al., 1997; Cheng et al., 2001; Cheng, 2003; Gaál-Nagy and Strauch, 2006), that suggest a linear relationship between the transformation pressure p and applied von Mises equivalent stress $S_\text{q} := \sqrt{3/2}\,\|\mathfrak{S}\|$. Transformation events during unloading appear on the force–displacement (P–h) curve (see Fig. 1) as jumps (pop-out) caused by the spontaneous formation of mc-Si or kinks (elbow) due to the formation of a-Si (cf. Domnich et al., 2000). Mixtures of a-Si and mc-Si have been observed even in the presence of pop-outs. In a more quantitative analysis, Zhang and Basak (2013) were able to relate the pop-out load to the amount of a-Si present in the transformation zone. By means of Raman spectroscopy investigations Kailer et al. (1997) found that lower unloading rates favor the formation of mc-Si, while only amorphous silicon is found for high unloading rates or small applied forces (<10 mN). In the latter case it was argued that the transformed volume is too small to accommodate the reconstructive β–Si → mc–Si transition. It appears that the unloading rate as well as the maximum applied force play a role, with the clear trend that fast contact loading at low loads leads to the formation of amorphous silicon. Reloading experiments show that, if an indent in which a-Si formed is subjected to repeated loading, the resulting load–displacement curves are closed (cf. Fujisawa et al., 2007; Pharr et al., 1990), provided that the unloading is fast enough. This confirms the finding that the a–Si → hda–Si transformation is reversible.

While slip bands are clearly visible in cross sectional transmission electron (XTEM) micrographs of indents (Bradby et al., 2000; Jian et al., 2010), dislocation plasticity only accounts for a minor portion of the inelastic deformation at room temperature (Bradby et al., 2002), because of silicon's high activation energy and resistance to dislocation motion (Gilman, 1993b). This is further highlighted by the temperature independence of the hardness of silicon up to ca. 800 K, where dislocation plasticity becomes the governing deformation mechanism (Domnich et al., 2008; Gilman, 1975; Suzuki and Ohmura, 1996; Vandeperre et al., 2007), as well as its lack of directional dependence. Giardini (1958) determined the Knoop hardness of Si for various directions in the (100), (110) and (111) planes and found the averaged values of 964 ± 0.5%,

---

[1] Bhuyan et al. (2012) recently presented some evidence for a reverse transformation from β-Si to cd-Si at elevated temperatures.

[2] Phase transformations in Si have been studied extensively by means of nanoindentation. Relevant works include (but are not limited to): Armstrong et al. (1996), Bradby et al. (2000, 2001, 2003), Callahan and Morris (1992), Clarke et al. (1988), Chang and Zhang (2009a,b,c, 2008), Chaudhri et al. (2007), Cook (2006), Domnich et al. (2000, 2008), Domnich and Gogotsi (2002), Fujisawa et al. (2008), Gerbig et al.(2011), Haberl et al. (2012)., Jang et al. (2005), Jian et al. (2010), Juliano et al. (2003, 2004), Khayyat et al. (2007), Kailer et al. (1997), Mann et al. (2000, 2002), Pharr et al. (1989, 1990, 1991, 1992), Puech et al. (2004), Rao et al. (2007), Ruffell et al. (2006, 2007a–c), Svechnikov et al. (2007), Vandeperre et al. (2007), Weppelmann et al. (1993, 1995), Wu et al. (1999), Zarudi et al. (2004), Zhang and Basak (2013), Zhang and Mahdi (1996), Zhang and Tanaka (1999), Zarudi and Zhang (1999), Zarudi et al. (2003, 2005).